Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for using Semipermeable Membrane Devices to Monitor Hydrophobic Organic Compounds in Surface Water

Version 1.1

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Although Ecology follows the SOP in most instances, there may be instances in which the Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
3/29/06	1.1	Revised section on PRC; editorial changes	6	Kirchmer/Kammin
3/30/06	1.1	Added language for Sections 4 and 7	4, 7	A. Johnson/Kammin

Environmental Assessment Program

Standard Operating Procedure for using semipermeable membrane devices (SPMDs) to monitor hydrophobic organic compounds in surface water.

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for using semipermeable membrane devices (SPMDs) to monitor hydrophobic organic compounds in surface water.[1]

2.0 Applicability

2.1 SPMDs are passive sampling devices used to concentrate a variety of hydrophobic organic contaminants from water. The passive sampling is based on membrane- and lipid-water partitioning. SPMDs may sample any nonionic organic compound with a K_{ow} value > 1, but, in practice, a chemical's K_{ow} should be greater than 300 (see Appendix A). The capability of the SPMDs to concentrate large concentrations of organic contaminants is a major advantage over traditional water sampling techniques, since lower detection limits are achievable when the samples are analyzed. SPMDs do not have many of the problems encountered in sampling biota, including lack of comparability between samples; metabolism and selective depuration are not an issue. SPMDs measure the dissolved and therefore readily bioavailable form of a contaminant. The ambient dissolved concentration can be estimated from the chemical concentration in the SPMD and ancillary data.

2.2 The average temperature during the deployment period must be known to calculate the dissolved concentration. The recovery of Performance Reference Compounds (PRCs) spiked into SPMDs prior to deployment is required to determine the PRC loss rates, which are used to correct for the effects of water velocity, turbulence, and biofouling on SPMD sampling rates. Total organic carbon data can be used to derive a total chemical concentration from the dissolved data.

3.0 Definitions

3.1 Environmental Sampling Technologies (EST) – Exclusive commercial supplier of SPMDs (http://www.est-lab.com/index.php).

3.2 K_{ow} – Octanol-water partitioning coefficient.

3.3 Performance Reference Compounds (PRCs) - Analytically non-interfering compounds with moderate to relatively high fugacity (escape tendency). PRCs are spiked into SPMDs prior to deployment.

[1] A variety of passive samples have been designed for monitoring environmental contaminants in surface water. The device described here is the most widely used and is standardized

3.4 Semipermeable membrane device (SPMD) – A passive sampler consisting of tubular, layflat, low-density polyethylene (LDPE) membranes containing a thin film of a high-molecular weight lipid (triolein). A standard SPMD consists of a 91 x 2.5 cm LDPE tube containing 1 mL of triolein (mass = 4.5 g, lipid volume = 0.001 L, membrane volume = 0.0037 L, SPMD volume = 0.0047 L).

3.5 Total Organic Carbon (TOC) – The amount of organically-bound carbon in a water sample.

3. 6 Triolein – Major nonpolar lipid found in aquatic organisms.

3. 7 TSU – Toxics Study Unit

4.0 Personnel Qualifications/Responsibilities

Personnel conducting field work using SPMDs should have prior experience doing water sampling and have a job classification equivalent to an Environmental Specialist 2 or higher.

5.0 Equipment, Reagents, and Supplies

5.1 Cans containing SPMD membranes mounted on spider carriers (Figure 1)
5.2 Stainless steel deployment canisters (Figure 2)
5.3 Coolers and blue ice
5.4 Paint can opener (rounded end)
5.5 Talc-free nitrile gloves
5.6 Zip ties
5.7 Deployment gear (anchors, stainless steel wire, swages, rope, buoys, etc)
5.8 Thermometer, Tid-bit, I-button, or other temperature monitoring device
5.9 Total organic carbon (TOC) sample bottles (optional)
5.10 Tools (rubber mallet, wire cutters, swaging tool, etc.)

Figure 1. SPMD Membrane on a Spider Carrier

Figure 2. Stainless Steel SPMD Deployment Canister (five-membrane capacity).

6.0 Summary of Procedure

6.1 SPMD Preparation and Handling Prior to Deployment

6.1.1. Consult with TSU, Manchester Laboratory, and EST staff to determine the appropriate number of membranes per sample to deploy. (Most TSU studies have used five membranes per sample. A greater or lesser number of membranes can be used depending on the chemicals being analyzed.)

6.1.2. Order appropriate number of membranes from EST.

6.1.3. The membranes are wound around spider carriers, placed in argon-filled one-gallon paint cans, and shipped frozen to the user. Each can holds up to three membranes. The membranes must be maintained at or near freezing. Be on hand to receive shipment from EST as soon as possible after arrival. Transfer the SPMDs directly to a freezer.

6.2 Deploying SPMDs

6.2.1 Prior to going into the field, wash each deployment canister with detergent and hot water, rinse with tap water, and air dry. Store the canisters in plastic bags.

6.2.2 Transport the cans containing the SPMDs in coolers. Blue ice is recommended as water ice causes the canisters to rust.

6.2.3 Upon arrival at the deployment site, unscrew the lid on the spider carrier can. Notice there is a threaded rod in the center of the device. The spider carrier will slide down this rod.

6.2.4 Work open the can with a paint can opener (screwdrivers, etc. deform and damage the lid).

6.2.5 Wear talc-free nitrile gloves, grasp the spider carrier by either the metal plate or center post, and lift it out of the can taking care not to damage or abrade the membrane. Avoid touching the membranes and do not touch the membranes with bare hands. Carefully reseal the cans using a rubber mallet to replace lids by light tapping on the edges.

6.2.6 Slide the carrier into the deployment canister. Make sure the threaded rod runs up through the carrier's center post (tube). A twisting motion sometimes helps the carrier slide down the rod.

6.2.7 If no spacers are called for and all the carriers are loaded, thread the lid back onto the canister. Start carefully to avoid cross-threading.

6.2.8 Be sure that the mounting ring on the lid matches its opposing ring on the canister body. Fasten the rings together with a zip tie so the lid does not unscrew during the deployment.

6.2.9 Attach a Tid-bit, I-button or other continuous temperature monitoring device to the canister if desired.

6.2.10 Because SPMDs are potent air samplers, exposure to air during deployment should be kept to a minimum – work quickly. Document the air exposure time in a field log.

6.3 Deployment Considerations and Options

6.3.1 Locate the SPMDs where they will be well hidden and yet can be found after deployment. Avoid strong currents which could damage or cause the loss of the device and avoid stagnant water. Allow for anticipated fluctuations in water level. (If exposed to air, the experiment is ruined.) Aim for a representative sample. Be aware of sources of contamination during deployment (engine exhaust, wind-blown dust, etc.).

6.3.2 A variety of techniques can be used to anchor the canisters. $1/8^{th}$ inch stainless steel cable and swages work well and provide some security. Here are four deployment options:

6.3.2.1 If the bottom is firm and not subject to siltation, the canister can be laid directly on the streambed and cabled to shore. If currents are strong, attach the canister to a concrete block. If siltation is a concern, raise the canister off the bottom.

6.3.2.2 Dams, docks, or other structures are convenient places to hang an SPMD. Attach a lead fishing weight if there are strong currents.

6.3.2.3 If vandalism and vessel traffic are not a concern, locate the SPMD at the desired depth between a surface buoy and anchor.

6.3.2.4 If vandalism or vessel traffic is a concern, use the Norton stealth deploy (Figure 3). Record sampling location carefully (landmarks and GPS) and retrieve with a grappling hook. A profiling depth sounder may be required to re-locate the snag line.

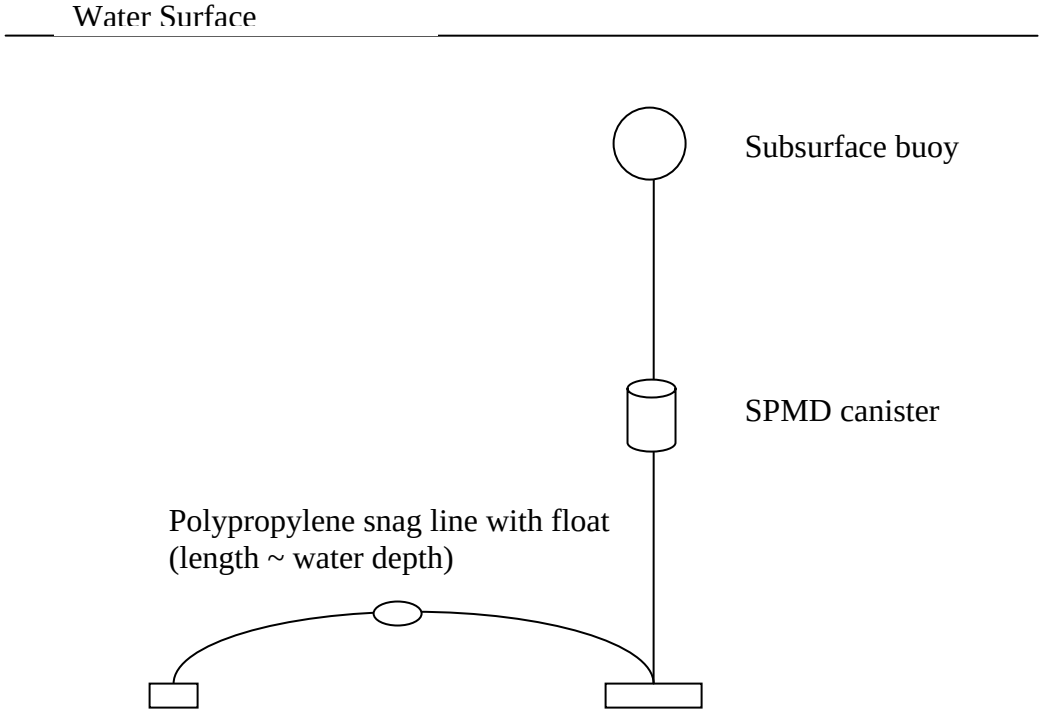

Figure 3. A Subsurface Deployment Method for SPMDs (Lower main anchor with loop of line through eye in snag anchor and pull to stretch snag line out before releasing. Retrieve with grappling hook.)

6..4 Performance Reference Compounds (PRCs)

6.4.1 The loss rate of PRCs is proportional to the uptake of target compounds. PRC loss rates in the field are used to derive an exposure adjustment factor (EAF) to recalibrate for the effects of temperature, water velocity, and biofouling on published SPMD sampling rates determined in the laboratory. A high rate of PRC loss translates into a lower calculated water concentration for target compounds because the chemical residues in the SPMD represent a larger volume of water, and vice versa.

6.4.2 PRC compounds may be spiked into all SPMD membranes or into one membrane for each deployment array. Selection of compounds to serve as PRCs is limited by the need to have measurable losses of PRC residues during exposure and the ability to differentiate PRC residues from other quality control standards, target compounds, and unknowns of potential interest. For studies where chlorinated pesticides and PCBs were analyzed, TSU has had good results using PCB-4 and PCB-29; 0.2 ug of each congener

per membrane for a five-membrane array. Isotopically-labeled compounds are also potentially useful PRCs (e.g., deuterated PAH). Avoid PRCs with high K_{ow} values as there may not be enough loss to quantify. Consult with EST, Manchester Laboratory, and experienced TSU staff to determine the appropriate compounds and spiking level.

6.5 Retrieval and Shipment to EST

6.5.1 A deployment period of approximately 28 days has generally afforded the best results. Consult with EST if a substantially longer or shorter deployment is desired.

6.5.2 The steps for retrieval are essentially the opposite of deployment. Wear nitrile gloves to remove the membranes and return them to the cans they were originally shipped in. Carefully reseal the cans using a rubber mallet. Label the cans appropriately and place in coolers with blue ice.

6.5.3 The SPMD extraction procedure (referred to as dialysis) is patented by EST. The SPMDs should be shipped to EST as soon after retrieval as possible or frozen for later shipment. Ship the SPMDs by FedEx to arrive the morning of the next business day and tell EST when to expect them. Include chain-of-custody forms and provide extra Manchester sample numbers for EST QC samples. Advise EST regarding any additional spiking required for the project, if clean-up of the extracts is desired, and if the extracts should be split to ship to different laboratories for analysis. Also, if the extracts are to be analyzed by isotope dilution mass-spectrometry, prior to shipping the SPMDs to EST they must be spiked with the isotopically-labeled internal standards (used for quantifying the target analytes).

6.6 Chemical Analysis.

6.6.1 Chemical analysis of SPMD extracts is beyond the scope of this SOP. EST will ship the extracts to Manchester laboratory or to contractors selected by Manchester. Be aware that a range of QC samples may apply depending on the laboratory and nature of the project. Consult with EST, Manchester Laboratory, and experienced TSU staff.

6.7 Data Analysis

6.7.1 Details on how SPMD data can be analyzed are provided in a tutorial by USGS (http://wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm). Here are a few basic concepts:

6.7.2 The absorbed amount of a chemical is proportional to the local water concentration. Therefore the environmental distribution and relative levels of contaminants can be assessed by directly comparing the absorbed amounts (residue per SPMD) among sites.

6.7.3 Estimating the dissolved concentration requires data on exposure time, exposure temperature, SPMD mass and volume, and published laboratory calibration data for the chemicals of interest (adjusted for PRC recovery). Because sampling rates correlate well with octanol-water partition coefficients (K_{ow}), sampling rates can also be estimated from laboratory calibration data for similar compounds when published rates

are not available. Equations are given in the USGS tutorial. A spreadsheet for calculating dissolved water column concentrations from SPMD data can be found at Y:\Shared\SPMDs. Correcting for the field blank is at the discretion of the project lead.

7.0 Records Management

For each site where SPMDs are deployed, the following data should be recorded in a field book:

- Site name
- Description of deployment location and method
- Number of SPMD membranes used
- Depth of SPMD from water surface
- Total depth of water
- Latitude and longitude of deployment site
- Date and time of deployment
- Date and time of retrieval
- Length of time SPMDs were exposed to air during deployment and retrieval
- Manchester Laboratory sample number assigned to the SPMDs
- Identifier for temperature monitoring device attached to the SPMDs
- Sample numbers, dates, and times of ancillary water samples (e.g., TSS and TOC)

8.0 Quality Control and Quality Assurance Section

8.1 Field Quality Control Samples

8.1.1 Field Blanks: Because SPMDs absorb air-borne contamination, field blanks are required for each set of deployments. EST refers to these as trip blanks. A field blank typically consists of the same number of SPMD membranes used in the samples. The field blank membranes are shipped in 1-quart paint cans. Expose field blanks to site atmosphere for a period equivalent to the average time the SPMD samplers were exposed during deployment and repeat for retrieval. The field blank does not need to be removed from the can. Carefully reseal the field blank can, label, and return to a cooler. Freeze at the earliest opportunity.

8.1.2 Ideally there is one field blank for each deployment site, but this is cost prohibitive for most studies. The number of blanks can be reduced by having a single blank represent similar types of sites. The number of blanks might be further reduced by limiting to one for the most contaminated site, or one for the least contaminated site, or by doing both to cover the range of potential blank contamination likely to occur in the samples.

8.1.3 Replicate Samples: Replicate samples consisting of SPMD canisters deployed side-by-side, or two or more canisters located in the same general vicinity should be included at the discretion of the project lead.

9.0 Safety

9.1 Field work done in connection with deploying and retrieving SPMDs should follow protocols described in the Environmental Assessment Program Safety Manual, paying special attention to those parts devoted to working on the water.

10.0 References

10.1 SPMDs were developed by the U.S. Geological Survey and are now of standardized design, patented, and commercially available only through Environmental Sampling Technologies (EST), St. Joseph, MO (http://www.est-lab.com/index.php). Details of SPMD theory, construction, and applications can be found at http://wwwaux.cerc.cr.usgs.gov/spmd/spmd_overview.htm.

Appendix A. Types of Chemicals Sampled by SPMDs

The following classes of compounds (not all-inclusive) have been shown to concentrate in SPMDs:

a. Polycyclic aromatic hydrocarbons (PAHs)
b. Polychlorinated biphenyls (PCBs)
c. Polychlorinated dioxins and furans (PCDDs/PCDFs)
d. Polybrominated diphenylethers (PBDEs)
e. Organochlorine pesticides
f. Several “new generation” pesticides (e.g., diazinon, chlorpyrifos, fenvalerate)
g. Pyrethroid insecticides
h. Nonyl phenols
i. Several herbicides and many industrial chemicals
j. Tributyltin
k. Akylated selenides